Enhancing Raman Signal Sufficiently for Practical Sensing Applications

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Abstract: Techniques are presented for enhancing weak Raman scattering signals for rapid yet accurate substance detection. Novel surfaces that allow signal enhancement quantification are described as are eye-safe methodologies that maximize the stand-off Raman detection range.
OCIS codes: (240.6695) Surface enhanced Raman scattering; (300.6450) Raman spectroscopy

1. Introduction

Developing rapid non contact means for efficient recognition and discrimination between explosives, volatile organic compounds (VOCs), and toxic gases is of significant interest to agencies responsible for security, law enforcement, air quality and environmental monitoring. Recent data [1] highlights the urgency of developing this capability with the number of fatalities and injuries resulting from undetected explosive devices continuing to increase at an alarming rate. Ideally, for this sensing technology to be practical it must offer rapid response, high sensitivity and the capability for remote substance detection. While the limit of detection requirement for a gas sensor depends on the particular application, sensitivity in the parts per billion level (with 1 ppb considered the canine limit of detection benchmark) is considered acceptable and the minimum required for the detection of VOCs in modern green buildings for air quality monitoring.

Currently, the presence of explosive vapours and chemical warfare agents can be measured with quartz crystal microbalances [2], gas chromatography [3], capillary electrophoresis [4], and ion mobility spectroscopy [5]. These methods, however, are laboratory based, not instantaneous, and require specific sample preparation. Lack of specificity and sensitivity are also limiting issues with these instrumentation complex techniques; and the signals obtained cannot distinguish between different components of the analyte. Raman spectroscopy[6] can overcome these limitations and has been used as a powerful 'fingerprinting' technique for more than 80 years as its molecular specificity is superior to alternatives and it does not require a carefully prepared sample to be taken from the measurement site for analysis in a laboratory. This makes the Raman technique particularly attractive for on-site detection and for real-time monitoring applications. However, as Raman spectroscopy is based on a weak inelastic scattering process, the number of Raman scattered photons are typically many orders of magnitude lower than the much stronger elastic (Rayleigh) component scattered by the sample. Therefore, developing a practical Raman sensing system for a specific application often requires devising strategies, such as introducing surfaces, that increase the Raman signal to a detectable level. Such strategies are essential for applications where the substance appears only in trace amounts (<1ppm) such as in the detection of explosive vapors, or when it is necessary to rapidly detect distant concealed substances.

Here we report on the techniques and strategies that we have developed to enhance Raman signals from target samples to allow practical detection. We describe two of the gold nanostructured surfaces that enhance the Raman scatter to allow detection of trace concentrations of various substances. In particular, we focus on a novel gold surface that acoustically enhances the Raman signal obtained from thiophenol adsorbed on the substrate. A unique feature of this sensor is that the Raman signal enhancement can be controlled simply by changing the acoustic wave amplitude, allowing the Raman signal enhancement factor to be directly measured with no variation in the concentration of the target compound. In addition, we describe the techniques that we developed to allow detection of concealed substances located at large distances from the operator. In particular we describe how the time-gated and spatially offset Raman approaches can overcome practical detection issues such as concealment, fluorescence, high levels of ambient light and eye-safety.

2. Surface enhanced Raman scattering

In 1974, it was shown that detection sensitivity could be dramatically increased by using nanostructured metallic surfaces to enhance the Raman signal by many orders of magnitude [7] making it possible to detect even single molecules [8]. Today, this technique of amplifying Raman spectra of material adsorbed to metallic surfaces is referred to as surface enhanced Raman scattering (SERS)[9] and covers a diverse range of approaches involving

metallic surfaces, thin films, roughened electrodes, nanoparticle aggregates, and so on, which can enhance the Raman signal anywhere up to 10^{12}.[10] This dramatic increase in signal is thought to result from plasmonic activity generated by the nanoscale features of the surface[11] as well as a smaller chemical enhancement effect[12].

A gold SERS sensor was fabricated by creating nanoscale ripples on a sapphire surface through exposure to femto-second laser pulses and then coating with gold [13]. Four different nitroaromatic vapours were tested at room temperature and concentrations in the range of 0.05 - 15 mM. An eight-fold increase in signal was observed on the structured portion of the surface over that observed on the unstructured portions. However, accurately measuring the Raman signal enhancement resulting from the surface structure of the ripple sensor is not straightforward, since it is difficult to accurately measure the sample concentration on the structured and unstructured portions of the substrate.

To separate the enhancement in Raman signal produced by a structured surface and produced by other effects such as variation in sample concentration, we developed a gold Raman sensor that creates controllable surface structures through interference of surface acoustic waves [14]. Since the sensor surface topology can be altered without variation of the sample concentration on the sensor surface, it is possible to directly correlate Raman signal enhancement with the structure of the gold sensor surface. As shown in Fig. 1, we observed a five-fold enhancement in the Raman signal intensity of a target analyte with this reusable Raman sensor .

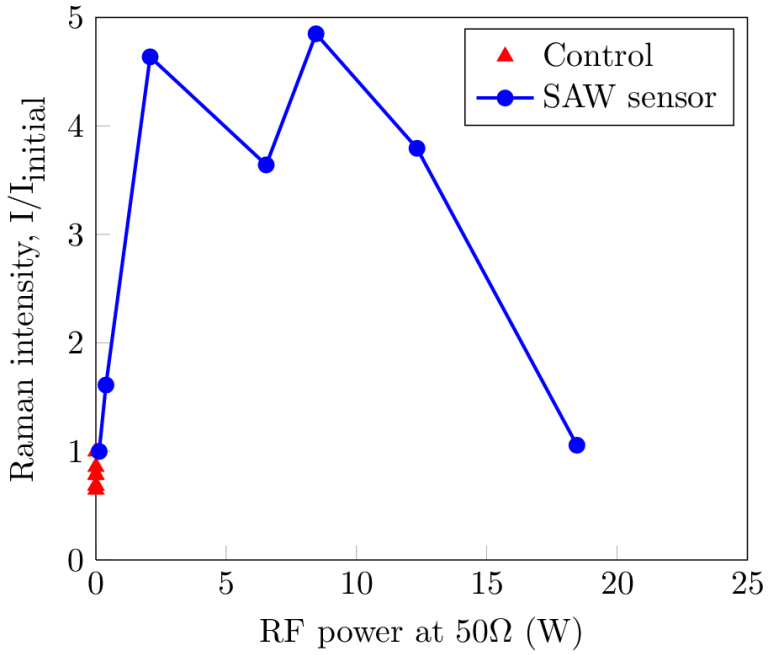

Fig. 1. Dependence of Raman signal enhancement on acoustic wave power

The sensor can also change the orientation of the analyte to clarify the presence or absence of bands in its Raman spectrum, and remove the physically adsorbed analyte without physical cleaning allowing it to be reused. This sensor can not only correlate metallic surface features with Raman signal enhancement, but also has the potential to establish the surface enhanced Raman scattering effect as the basis of a reusable and reliable Raman sensor for commercial real-time monitoring applications including the on-site detection of explosive vapors.

3. Stand-off Raman spectroscopy

Methods that are currently used for explosive detection suffer from limitations such as requiring long signal acquisition times, or the need for operators to be in close proximity to the potential hazard. Clearly a more preferable approach is to use a technique that is capable of detecting explosives from safe operator distances over realistic timescales. Stand-off Raman spectroscopy is a method which can detect substances more than 100 m away in less than a second. In addition, as it is an optical technique, detection occurs without making physical contact with the sample, reducing the risk of accidental detonation. However, to be effective several practical limitations must be overcome.

Here we show how time-gated detection of the Raman scatter produced when laser pulses are incident on the target allows for the removal of unwanted fluorescence and Raman scatter from a vessel containing the target material, and how the approach can be extended to depth-profile analysis of the package [15]. We also describe how spatially offset detection can be used to separate the desired sample signal from undesired signals from contaminants

under conditions of high ambient background light [16]. Since the maximum stand-off distance at which a Raman signal can be detected increases with incident laser power, the operating range of stand-off Raman system can be easily increased. Unfortunately, laser radiation has the potential to injure the eye and or skin if the power density is too great, and as a result the use of high power accessible laser beams in public places is heavily regulated. Here we show that the safe exposure levels to laser light are 1000 times greater than in the visible and as a result greater Raman signal intensity is possible with safe levels of laser light at UV wavelengths as shown in Figure 2. As a result, it is possible to generate Raman signals from nitroaromatics using safe levels of UV light that are detectable even when located many metres from the detector.

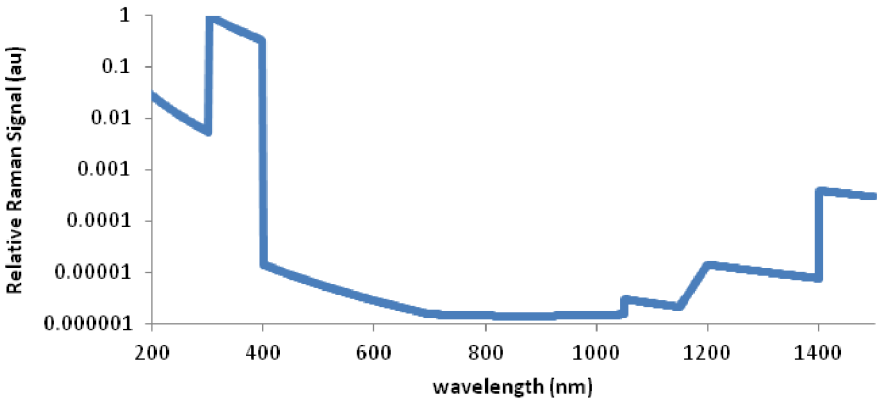

Fig. 2. Relative Raman signal at safe exposure levels at different wavelengths

4. References

[1] National Consortium for START, "Annex of Statistical Information-Country Reports on Terrorism 2013 " Technical Report (2014).

[2] G. Bunte, J. Hurttlen, H. Pontius, K. Hartlieb, H. Krause, Chim. Acta, **591,** 49 (2007).

[3] R. Battle, H. Carlsson, P. Tollback, A. Colmsjo, C. Crescenzi, Anal. Chem. **75,** 3137 (2003).

[4] T. Kishi, J. Nakamura, H. Arai, Electrophoresis **19,** 3 (1998).

[5] D. Fetterolf, T. Clark, J. Forensic Sci. **38,** 28 (1993).

[6] C. Raman, K. Krishnan, Nature **121,** 501 (1928).

[7] M. Fleischmann, P. Hendra, A. McQuillan, Chem. Phys. Lett. **26,** 163 (1974).

[8] K. Kneipp, Y. Wang, H. Kneipp, L. Perelman, I. Itzkan, R. Dasari, M. Field, Phys. Rev. Lett. **78,** 1667 (1997).

[9] D. Jeanmarie, R. Van Duyne, J. Electroanal. Chem. **84,** 1 (1997).

[10] S. Bioletti, R. Leahy, J. Fields, B. Meehan, W. Blau, , J. Raman Spec. **40,** 1043 (2009).

[11] A. Henry, J. Bingham, E. Ringe, L. Marks, G. Schatz, R. Van Duyne , J. Phys. Chem. C **115,** 9291 (2011).

[12] A. Campion, J. Ivanecky, C. Child, M. Foster, J. Am. Chem. Soc. **117,** 11807 (1995).

[13] A. Chou, E. Jaatinen, R. Buividas, G. Seniutinas, S. Juodkazis, E. Izake, P. Fredericks, Nanoscale **4,** 7419 (2012).

[14] E. Jaatinen, M. Adams, A. Chou, N. McKay-Parry,P. Fredericks , J. Raman Spec. **45,** 636 (2014).

[15] S. Sundarajoo, E. Izake, W. Olds, B. Cletus, E. Jaatinen, P. Fredericks, J. Raman Spec. **44,** 949 (2013).

[16] E. Izake, B. Cletus, W. Olds, S. Sundarajoo, P. Fredericks, E. Jaatinen, Talanta **94,** 342 (2012).